SYSTEMS AND METHODS FOR CONTROLLING THE
ACTIVITY OF CARBON IN HEAT TREATING ATMOSPHERES

RELATED APPLICATION

This application is a continuation of co-pending
U.S. Application Serial No. 09/252,158 filed 18 February
1999.

FIELD OF THE INVENTION

This invention relates generally to the
monitoring and/or control of atmospheres within heat
treating furnaces.

BACKGROUND OF THE INVENTION

Steel parts can undergo a process called
carburizing or neutral hardening inside a heat treating
furnace. Inside the furnace, the steel parts are exposed
to prescribed high temperature conditions in the presence
of a specially formulated, carbon-enriched gas
atmosphere.

Most heat treating atmospheres contain carbon
monoxide (CO), carbon dioxide (CO_2), methane (CH_4),
hydrogen (H_2), and water vapor (H_2O). The relative amounts
of these gases in the atmosphere depend upon the type of
carrier gas used, the processing temperatures, and the
amount of enriching gas added during processing.

For example, an endothermically generated gas,
produced by catalytic cracking of natural gas in the

presence of air, typically contains the following nominal
ranges (expressed in % by volume) of gas constituents:

$CO \approx 20\%$	$CO_2 \approx 0.1\%$ to 0.5%
$H_2 \approx 40\%$	$H_2O \approx 0.2\%$ to 1.2%
$N_2 \approx 40\%$	$CH_4 \approx 0.2\%$ to 0.8%

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In gas carburization, a common commercial
practice is to use an endothermic gas carrier enriched
with natural gas or propane. The process variables used
to monitor and control the carburization process using
this type of atmosphere include (i) the carbon potential
of the heat treating atmosphere (expressed as a weight
percent of carbon), (ii) the temperature of the heat
treating furnace, and (iii) the processing time.

For a given temperature condition, the reactions
that transfer carbon to the surface of the steel part are
maintained by keeping the carbon potential of the gas
atmosphere within a defined range. For example, if the
carbon potential of the furnace atmosphere is greater
than the carbon potential of the surface of the steel
parts being processed, carburization occurs, i.e., carbon
is transferred from the gas atmosphere to the surface of
the steel parts. Increasing the carbon potential of the
gas atmosphere increases the rate of carburization.
However, if the carbon potential of the atmosphere at a
given temperature exceeds a critical value beyond the
defined range, sooting occurs. Likewise, if the carbon
potential of the atmosphere at a given temperature is
less than the carbon potential of the surface of the
steel parts being processed, decarburization occurs,
i.e., carbon is transferred from the surface of the steel
parts to the gas atmosphere.

The desired condition for neutral hardening is
one in which the carbon potential of the atmosphere is
equal to the carbon potential of the surface of the steel

parts being processed. In this case, no carbon is transferred between the surface of the steel parts and the furnace atmosphere.

Further details regarding the concept of the carbon potential and the kinetic conditions for transfer of carbon between the surface of the steel part and the furnace atmosphere are found in Blumenthal, "Control of Endothermic Generators - A Technical Comparison of Endothermic and Nitrogen/Methanol Carrier Atmosphere," *Heat Treating Proceedings (16th ASM Heat Treating Society Conference & Exposition), 19-21 March 1998*, pp. 19 to 25.

The carbon potential of an atmosphere with a fixed carbon monoxide concentration can be ascertained by measuring the partial pressure of carbon dioxide (P_{CO2}) in the atmosphere, using infrared analysis. This, however, requires sampling the gas from the furnace atmosphere and cooling it to room temperature. Sampling errors arise, due to possible leaks in the gas sampling line, alteration of the gas chemistry due to sooting, or the water-gas shift due to cooling, or a combination of these events. These sampling errors inherent in remote gas sampling are difficult to eliminate.

For this reason, a more common method for assessing the carbon potential has entailed the use of an *in situ* oxygen sensor used in association with a thermocouple.

The oxygen sensor is typically installed in the heat treating furnace in direct contact with the heated gas carburizing atmosphere. This obviates the sampling errors, described above, which are inherent in remote gas sampling techniques. The sensor includes a solid electrolyte. One side of the electrolyte contacts the carburizing atmosphere to be measured. The other side of the electrolyte contacts a reference gas, whose oxygen content is known.

A voltage (measured in millivolts) E(mv) is generated between the two sides of the electrolyte. The magnitude of this voltage E (mv) is a function of the temperature (sensed by the thermocouple) and the

5 difference between the oxygen content in the carburizing atmosphere and the oxygen content in the reference gas. The voltage E(mv) can be expressed as follows:

$$E(mv) = 0.0496T \times \log \frac{P_{O2}(Ref)}{P_{O2}} \qquad (1)$$

where:

T is the sensed temperature (in degrees Kelvin

10 °K).

P_{O2} (Ref) is the known partial pressure of oxygen in the reference gas, which in the illustrated embodiment is air at 0.209 atm. Other reference gases can be used.

P_{O2} is the partial pressure of oxygen in the heat

15 treating atmosphere.

Knowing the oxygen content of the reference gas [P_{O2} (Ref)], one can determine the oxygen content of the furnace atmosphere [P_{O2}] by measuring the probe voltage [E(mv)] and the temperature T(°K). Knowing the carbon

20 monoxide content of the carrier gas (which can be pre-set or separately measured by infrared analysis), the isothermal relationship between the oxygen probe voltage output and carbon potential can be experimentally ascertained and plotted for different temperature

25 conditions. In this way, the carbon potential can be directly related to the oxygen probe voltage and temperature.

Further details of this relationship between oxygen probe voltage and carbon potential are found in

30 the above-identified article by Blumenthal.

In use, a controller associated with the heat treating furnace compares the carbon potential of the furnace atmosphere to a "set point" carbon potential,

which is selected to reflect a targeted carbon potential. The controller controls the addition of an enriching gas, such as natural gas, into the atmosphere to maintain the carbon potential of the atmosphere at the set point, and thereby maintain the desired carbon potential in the atmosphere.

The control of carbon potential is only meaningful when the steel being processed is in a single phase field, i.e., austenite. This single phase field occurs only at elevated temperatures and is dependent on the alloy content, the carbon content of the steel, and the temperature.

There are other, lower temperature heat treating applications, e.g., spherodize annealing. In spherodize annealing, the objective is to create a two phase region, where the microstructure of the steel being processed comprises spherical-shaped particles of iron carbide(cementite)(Fe_3C) distributed in a matrix of alpha iron (ferrite) (α-Fe). This ferrite and iron carbide microstructure produces a steel that is very ductile and easily deformable by plastic deformation. The steel fastener industry, for example, depends upon steel that is in the spherodize annealed condition.

Fig. 1 shows a typical iron-carbon binary phase diagram for hypoeutectoid and hypereutectoid plain carbon steel compositions possessing different weight percentages of carbon. The diagram shows that there is a critical temperature A_1 (about 1333°F) at which the desired two phase ferrite and iron carbide microstructure exists for both hypoeutectoid and hypereutectoid compositions. The most commercially practical spherodize annealing rates exist at or near the temperature A_1. This preferred region is shaded in Fig. 1.

Below A_1, the rate of spherodize annealing decreases with decreasing temperature for both

hypereutectoid and hypoeutectoid compositions. At or below a temperature of about 1250°F, the decreased rate becomes commercially impractical.

For hypoeutectoid compositions (i.e., with weight percent carbon below about 0.8), Above the temperature A_1, equilibrium phases of austenite (γ- Fe) and ferrite occur, until the temperature exceeds A_3. Above the temperature A_3, single phase austenite forms, and spherodize annealing conditions cease. As Fig. 1 shows, the temperature corresponding to A_3 varies according to the weight percent carbon of the hypoeutectoid composition.

For hypereutectoid compositions (i.e., having weight percent carbon above about 0.8), equilibrium phases of austenite and iron carbide form above the temperature A_1, until the temperature reaches A_{CM}. Above A_{CM}, single phase austenite forms. As Fig. 1 shows, the temperature corresponding to A_{CM} varies according to the weight percent carbon of the hypereutectoid composition.

During spherodize annealing, the objective is to provide a gas atmosphere that does not carburize or decarburize or oxidize the steel parts. The purpose of spherodize annealing is to produce the particular two-phase microstructure just described.

In the spherodize annealing process, the relative amounts of the two phases, e.g., ferrite and iron carbide, must remain unchanged. Thus, the heat treating atmosphere must be close to equilibrium with the two-phase ferrite and iron carbide. The atmosphere must be properly maintained to prevent either carburization (i.e., the conversion of ferrite with carbon from the atmosphere to produce iron carbide) or decarburization (i.e., the conversion of iron carbide to ferrite resulting from the removal of carbon by the atmosphere). The atmosphere must also prevent oxidation of the steel

parts.

Carbon potential is meaningful only in a single phase region. Thus, the carbon potential is not an appropriate process variable for controlling the two-phase spherodize annealing process.

The activity of carbon (or A_c) can be used as a process variable to control the furnace atmosphere to achieve the objectives of spherodize annealing. When the A_c of a furnace atmosphere is equal to the A_c of the two phase mixture of ferrite and iron carbide, the atmosphere is in equilibrium with the steel parts. In the equilibrium condition, there is no transfer of carbon between the steel and the furnace atmosphere.

A_c is a function of the partial pressure of carbon monoxide (P_{co}) and the partial pressure of carbon dioxide (P_{co2}) at a given temperature condition. A_c can be expressed as follows:

$$A_c = K_1(P_{CO} / P_{CO2})P_{CO} \qquad (2)$$

where K_1 is the thermodynamic constant of the reaction $2CO = \underline{C} + CO_2$, which occurs during an exchange of carbon between the furnace atmosphere and the steel parts,

where:

CO is carbon monoxide, CO_2 is carbon dioxide, and $\underline{C}$ represents carbon in solution in iron.

A_c may also be represented by the following equation:

$$A_C = \frac{K_1}{100} \times \frac{(\% CO)^2}{\% CO_2} \qquad (3)$$

where %CO is the percent carbon monoxide in the furnace atmosphere, and $\%CO_2$ is the percent of carbon dioxide in the furnace atmosphere.

There are atmospheres used for spherodize annealing of steel rod and wire, where relatively high

concentrations of carbon monoxide are present, e.g., mixtures of exothermic and endothermic gases; mixtures of nitrogen and endothermic gases; and mixtures of nitrogen and methanol. These atmospheres are described in Stanescu, "Principal Annealing Atmospheres for Steel Rod and Wire," *Wire Journal® International*, pp. 79-83, June 1991.

In these carbon monoxide-rich atmospheres, the %CO and %CO$_2$ values in the atmosphere can be measured by removing atmosphere from the furnace for infrared analysis at room temperature. As already discussed, this technique is prone to many sampling errors. Nevertheless, in these carbon monoxide-rich atmospheres, the absolute value of the sampled ratio [(%CO)^2 / %CO$_2$] can be at least quantified in some manner, albeit inexactly. The sampled ratio is proportional to A_c, by virtue of the thermodynamic constant K_1. The relationship between the sampled ratio and A_c can be experimentally determined for a given set of operating conditions.

In use, a controller compares the measured ratio to a set point value. Based upon the comparison, the controller can govern the mixing of appropriate gases to keep the ratio at the designated set point value.

Nevertheless, the use of a sampled ratio [(%CO)^2 / %CO$_2$] as an indication of A_c is, at best, not exact and subject to a whole host of sampling errors. It also requires the presence of an atmosphere with a high concentration of carbon monoxide (i.e., "richer"), to enable the infrared analysis to be conducted in the first instance. These carbon monoxide-rich atmospheres are expensive to generate, highly kinetically reactive, and require the high degree of monitoring and control.

Atmospheres lower in carbon monoxide concentration (i.e., "leaner") are well suited for use in applications where two phase regions exist, such as

spherodize annealing. For example, as described in the above identified Stanescu article, carbon monoxide-lean atmospheres can be produced for spherodizing steel rod and wire by mixing nitrogen with a hydrocarbon (e.g., propane or propylene). The leaner atmospheres tend to be cheaper to generate, less kinetically reactive, and do not require the tight control that carbon monoxide-rich atmospheres require. However, due to the relatively low concentrations of carbon dioxide present in leaner atmospheres, the measurement of $\%CO_2$ by infrared analysis becomes, at best, problematic.

For example, at 1333° F, $K_1 = 0.457$, and if $\%CO = 1\%$ and $A_c = 1$, then, according to Equation (3), $\%CO_2 = 0.0046\%$. The highest accuracy of a conventional CO_2 analyzer is $\pm 0.002\%$. It can thus be seen that, in these carbon monoxide-lean atmospheres, the accurate assessment of the activity of carbon from infrared measurements of $\%CO$ and $\%CO_2$ is not possible. Therefore, when a nitrogen-hydrocarbon atmosphere is used and the percent carbon monoxide is less than one percent, there exists no commercially viable way to accurately assess the activity of carbon during a spherodize annealing process.

In summary, to acquire even an error-prone sample ratio $[(\%CO)^2 / \%CO_2]$ requires the presence of an expensive, highly reactive, carbon monoxide-rich atmosphere(e.g., a nitrogen/endothermic atmosphere). In cheaper, less reactive, carbon monoxide-lean atmospheres(e.g., a nitrogen-hydrocarbon atmosphere), it is possible to acquire only a rough estimation of the activity of carbon for control purposes.

SUMMARY OF THE INVENTION

One aspect of the invention provides systems and methods for monitoring the activity of carbon in a heat treating atmosphere, e.g., where a two phase region is desired for spherodize annealing. The systems and methods

generate a computed activity of carbon value for the gas atmosphere from at least one sensor placed *in situ* in the gas atmosphere.

Another aspect of the invention provides systems and methods for generating as a function of temperature, partial pressure of oxygen, and carbon monoxide content of the gas atmosphere, and without determining a carbon dioxide content of the gas atmosphere.

The systems and methods can make use of the computed activity of carbon value, e.g., to control the gas atmosphere.

In a preferred embodiment, the systems and methods compare the computed activity of carbon output to a set point activity of carbon value and generate a control signal based upon the comparison. In a preferred embodiment, the selected activity of carbon value is approximately one.

The invention makes possible the realization of accurate and reliable assessment of the activity of carbon in any two phase region, regardless of the carbon monoxide concentration of the atmosphere and without requiring a remote and error-prone analysis of the percent carbon dioxide. Other features and advantages of the inventions are set forth in the following Description and Drawings, as well as in the appended Claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a typical prior art *iron-carbon* binary phase diagram for plain carbon steel compositions, identifying the temperature region conducive to spherodize annealing;

Fig. 2 is a schematic view of a system for heat treating metal, which includes a processing module for deriving an activity of carbon value as a function of *in situ* temperature and a voltage signal from an *in situ*

oxygen sensor;

Fig. 3 is a side view, with portions broken away and in section, exemplifying one of the types of *in situ* temperature and oxygen sensors, which can be coupled to the processing module shown in Fig. 2;

Fig. 4 is a representative plot showing the relationship between A_c and temperature for a two phase condition of ferrite (α-Fe) and iron carbide (Fe_3C) or ferrite (α-Fe) and austenite (γ-Fe) for hypoeutectoid plain carbon steel;

Fig. 5 is a representative plot showing the relationship of the onset of oxidation to the outputs of an oxygen sensor over a range of temperatures;

Fig. 6 is a representative screen of a graphical user interface to display information processed by the processing function for the furnace shown in Fig. 2;

Fig. 7 is a screen of the data shown in Fig. 6, with the data recorded in a trend format; and

Fig. 8 is the screen of the data shown in Fig. 6, with the data displayed in a unit data format.

The invention may be embodied in several forms without departing from its spirit or essential characteristics. The scope of the invention is defined in the appended claims, rather than in the specific description preceding them. All embodiments that fall within the meaning and range of equivalency of the claims are therefore intended to be embraced by the claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 2 shows a system 10 for controlling the atmosphere of a heat treating furnace 12 of the type used for spherodize annealing. Fig. 2 schematically shows the furnace 12 for the purpose of illustration, as the details of its construction are not material to the invention. The furnace 12 can comprise, e.g., a conventional batch, Short Time Cycle (STC) furnace of the

type discussed in Powers et al., "Process Control for Short Time Cycle Spherodize Annealing," *Salem Furnace Company*.

The furnace 12 includes a source 14 of the desired heat treating atmosphere, which is conveyed into the furnace 12. The furnace 12 also includes a source 16 of heat for the furnace 12. The source 16 heats the interior of the furnace 12, and thus the heat treating atmosphere itself. The heated atmosphere reacts with steel parts within the furnace 12 to produce a spherodize microstructure, as previously described.

A temperature sensor S, e.g., a thermocouple, is electrically coupled to a furnace temperature controller 26, which is itself coupled to the heat source 16. The furnace temperature controller 26 compares the temperature sensed by the sensor S to a desired value set by the operator (using, e.g., an input device 28). The furnace temperature controller 26 generates command signals based upon the comparison to adjust the amount of heat provided by the source 16 to the furnace 12, to thereby maintain the desired temperature.

The system 10 includes a processor 18 for monitoring or controlling the activity of carbon A_c of the atmosphere at the temperature maintained in the furnace 12, to thereby prevent or minimize carburization, decarburization, sooting, or oxidation on the surface of the parts.

According to one aspect of the invention, the processor 18 need not include any remote gas analyzer. Instead, the processor 18 can include only an *in situ* temperature sensor 20 and an *in situ* oxygen sensor 22. The processor 18 also includes a microprocessor controlled processing function 24, which is electrically coupled to the temperature and oxygen sensors 20 and 22.

The oxygen sensor 22 can be variously

constructed. In Fig. 2, the oxygen sensor 22 is of the type described in U.S. Patent No. 4,588,493 ("the '493 patent"), entitled "Hot Gas Measuring Probe." The '493 patent is incorporated into this Specification by reference.

The oxygen sensor 22 is installed through the wall 30 in the furnace 12. The oxygen sensor 22 is thereby exposed to the same temperature and the same atmosphere as the metal parts undergoing processing.

As Fig. 3 shows, the oxygen sensor 22 includes an outer sheath 32, which, in the illustrated embodiment, is made of an electrically conductive material. Alternatively, the sheath 32 could be made of an electrically non-conductive material.

The sheath 32 encloses within it an electrode assembly. The electrode assembly comprises a solid, zirconia electrolyte 34, formed as a hollow tube, and two electrodes 36 and 38.

The first (or inner) electrode 36 is placed in contact with the inside of the electrolyte tube 34. A reference gas occupies the region where the inside of the electrolyte 34 contacts the first electrode 36. The oxygen content of the reference gas is known.

The second (or outer) electrode 38, which also serves as an end plate of the sheath 32, is placed in contact with the outside of the electrolyte tube 34. The furnace atmosphere circulates in the region where the outside of the electrolyte 34 contacts the second electrode 38. The furnace atmosphere circulates past the point of contact through adjacent apertures 40.

A voltage E (mv) is generated between the two sides of the electrolyte 34. As previously explained, and as expressed in Equation (1), the magnitude of E (mv) is related to the temperature and the difference between the oxygen content in the furnace atmosphere and the oxygen

content in the reference gas.

The voltage-conducting lead wires 42(+) and 42(-
)are coupled to the processing function 24.
Alternatively, when an electrically non-conductive sheath
32 is used, internal lead wires (not shown) are coupled
to the second electrode 38 to conduct the voltage E (mv)
to the processing module 24.

Other types and constructions for the oxygen
sensor 22 can be used. For example, the oxygen sensor 22
can be of the type shown in U.S. Patent No. 4,101,404.
Commercial oxygen sensors can be used, e.g., the
CARBONSEER™ or ULTRA PROBE™ sensors sold by Marathon
Monitors, Inc., or ACCUCARB® sensors sold by Furnace
Control Corporation. Some oxygen sensors are better
suited for use in higher temperature processing
conditions, while other oxygen sensors are better suited
for lower temperature processing conditions.

In the illustrated embodiment, the temperature
sensor 20 takes the form of a thermocouple. Preferably,
the temperature sensor 20 is carried within the
electrolyte tube 34, e.g., by a ceramic rod 35. In this
arrangement, the ceramic rod 35 includes open interior
bores 37, through which the reference gas is introduced
into the interior of the electrolyte tube 34. The lead
wire 42(+) for the oxygen sensor 22 passes through one of
the bores 37, and the other lead wire 42(-) for the
oxygen sensor 22 is coupled to the sheath 32. The lead
wires 39(+) and 39(-) for the thermocouple sensor 20 pass
through the other bores 37, to conduct the thermocouple
voltage output t (mv) to the processing function 24.

By virtue of this construction, the temperature
sensor 20 is exposed to the same temperature conditions
as the furnace atmosphere circulating past the point of
contact of the electrolyte 34 and electrodes 36 and 38.
This is also essentially the same temperature condition

as the metal parts undergoing treatment.

Alternatively, the temperature sensor 20 can comprise a separate sensor, which is not an integrated part of the oxygen sensor 22. The thermocouple S, used in association with the heat source 16, can also be used to sense temperature conditions for use in association with the oxygen sensor 22.

The processing function 24 includes a resident algorithm 44. The algorithm 44 computes the activity of carbon A_c as a function of temperature of the atmosphere, oxygen partial pressure of the atmosphere, and carbon monoxide partial pressure of the atmosphere.

The input indicative of the carbon monoxide partial pressure in the atmosphere in the furnace can be generated in various ways. The input can be provided, e.g., by a remote infrared sensor 60 (shown in Fig. 2), which communicates with the furnace 12 through a gas sampling tube 62 installed through the furnace wall 30. The infrared sensor 60 analyses the sampled gas atmosphere at room temperature to ascertain the %CO. The sensor 60 conveys a voltage input to the processing function 24.

Alternatively, however, the carbon monoxide content of the atmosphere gas can be ascertained in accordance with the invention without need for the remote sensor 60. For example, the carbon monoxide content of the atmosphere can be preset by the operator using, e.g., an input 64 to the atmosphere source 14. The preset input 64 is also conveyed to the processing function 44.

Still alternative, as will be described in greater detail later, in atmospheres formed from a mixture of nitrogen and an endothermic atmosphere, or a mixture of nitrogen and methanol, the partial pressure of carbon monoxide can be expressed as a function of E (mv) from the oxygen sensor 22 and t (mv) from the temperature

sensor 20, without need of remote sensing of carbon monoxide.

The resident algorithm 44 is based upon the activity of carbon for the following reaction:

$$CO = \underline{C} + \tfrac{1}{2}O_2 \quad (4)$$

where:

CO is carbon monoxide.

$\underline{C}$ is the carbon in solution in iron.

O_2 is oxygen.

The activity of carbon A_c for this reaction can be expressed as follows:

$$A_C = (K_2)P_{CO} / (P_{O2})^{1/2} \quad (5)$$

where:

P_{CO} is the partial pressure of carbon monoxide in the gas atmosphere.

P_{O2} is the partial pressure of oxygen in the gas atmosphere.

K_2 is the thermodynamic constant for the reaction of Equation (4).

K_2 can also be expressed exponentially, as follows:

$$K_2 = e^{-[\frac{27,000+20.95T}{1.9872T}]} \quad (6)$$

where:

T is the temperature sensed by the temperature sensor 20, in °K.

The partial pressure of oxygen P_{O2}, in turn, is related to the voltage signal E(mv) of the oxygen sensor 22, as expressed in Equation (1), previously described.

By algebraic substitution of variables in Equations (1), (5), and (6), an expression for A_c can be derived as a function of E (mv), the sensed or preset partial pressure of carbon monoxide P_{CO}, and mv-

temperature signal t(mv), expressed as temperature T in °K, as follows:

$$A_C = e^{-\left[\frac{27,000+20.95T}{1.9872T}\right]} P_{CO}(2.1874)10^{\frac{E(mv)}{0.0992T}} \quad (7)$$

The algorithm applies Equation (7) to derive the activity of carbon A_C. In this way, the processing function derives the activity of carbon A_C without directly determining the absolute value of P_{CO2}. As the absolute CO_2 content of the atmosphere is not a constraining variable, the processing function 24 can derive the activity of carbon A_C by applying Equation (7) in both rich carbon monoxide and lean carbon monoxide atmospheres. Application of the Equation (7) makes possible the accurate control of the activity of carbon A_C in all atmospheres, including leaner, less reactive atmospheres, where greater variations in the carburizing environment can be tolerated without the sudden onset of sooting or decarburizing conditions.

The factor P_{CO} in Equation (7) can be inputted to the processing function 24 in various ways. For example, as already described, remote infrared sensing can be used.

Alternatively, when an atmosphere formed from a mixture of nitrogen and an endothermic atmosphere is used, the flow rate of nitrogen and the endothermic atmosphere introduced into the furnace 12 can individually be set at a fixed rate. In this circumstance, the partial pressure of carbon monoxide can also be expressed as a function of E (mv) from the oxygen sensor 22 and t (mv) from the temperature sensor 20, without need of remote sensing. In this arrangement, the activity of carbon A_C can be derived solely based upon the output of the oxygen sensor 22 and thermocouple 22, without requiring the use of a separate carbon monoxide sensing sensor or independently controlling the carbon

monoxide content of the atmosphere.

More particularly, when the flow rates of nitrogen and the endothermic atmosphere or nitrogen and methanol atmosphere are fixed, the sum of the partial pressures of carbon monoxide and carbon dioxide will equal a constant quantity H, therefore:

$$P_{CO} + P_{CO_2} = H \quad (8)$$

The partial pressure of carbon monoxide P_{co} can therefore be expressed, as follows:

$$P_{CO} = H - P_{CO_2} \quad (9)$$

Given the thermodynamic reaction:

$$CO + \tfrac{1}{2}O_2 = CO_2 \quad (10)$$
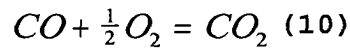
the thermodynamic equilibrium constant K_3 can be expressed as:

$$K_3 = \frac{P_{CO2}}{P_{CO}(P_{O2})^{1/2}} \quad (11)$$

K_3 can also be expressed exponentially, as follows:

$$K_3 = e^{-\Delta G^o_{10}/RT} \quad (12)$$

where:

the quantity:

$$\Delta G^o_{10}$$

is the standard free energy for Equation (10), expressed in calories per mole as follows:

$$\Delta G^o_{10} = -67{,}495 + 20.758T \quad (13)$$

R is the gas constant (i.e., 1.9872 cal/mole$^{-\circ K}$), and

T is the temperature in °K.

From the Expression (11), the ratio of the partial pressures of carbon dioxide and carbon monoxide

can be derived as a function of the thermodynamic constant K_3 and the partial pressure of oxygen, as follows:

$$K_3(P_{O2})^{1/2} = \frac{P_{CO2}}{P_{CO}} \quad \textbf{(14)}$$

5   Combining Equations (9) and (14), the following expression for P_{CO} is derived:

$$P_{CO} = \frac{H}{1 + K_3 P_{O2}{}^{1/2}} \quad \textbf{(15)}$$

The partial pressure of oxygen P_{O2} in Equation (15) can, in turn, be related to the E (mv) output of the 10   oxygen sensor 22 and the t (mv) output of the thermocouple 20, expressed as temperature T in °K, as follows:

$$(P_{O2})^{1/2} = 0.4572(10^{-E(mv)/0.0992T}) \quad \textbf{(16)}$$

By algebraic substitution of variables in expressions (12), (13), (15), and (16), the partial 15   pressure of carbon monoxide P_{CO} can also be expressed as a function of the E (mv) output of the oxygen sensor 22 and the t (mv) output of the thermocouple 20, expressed as temperature T in °K, as follows:

$$P_{CO} = H\left[\frac{1}{1 + (e^{-\Delta G_{10}^o/RT})(0.4572)(10^{-E(mv)/0.0992T})} \right] \quad \textbf{(17)}$$

20   or, alternatively:

$$P_{CO} = H\left[\frac{1}{1 + e^{\left[\frac{67,495-20.7587}{1.9872T}\right]}(0.4572)(10^{\frac{-E(mv)}{0.0992T}})} \right] \quad \textbf{(18)}$$

To supply the input variables E (mv) and t (mv) to the algorithm 44, the processing function 24 is electrically coupled to the lead wires 42(+) and 42(-) of 25   the oxygen sensor 22 and the lead wires 39(+) and 39(-) of the temperature sensor 20. An input reflecting the partial pressure of CO is also supplied in the manners previously described, or as derived directly from

electrical inputs E (mv) and t (mv), expressed as temperature T in °K. The electrical inputs are supplied to the algorithm 44, which provides, as an output, the quantity A_c according to Equation (7). The output

5   expresses the magnitude of the activity of carbon A_c.

Unlike prior systems, the system 10 requires no measurement of the carbon dioxide content by remote sensing at ambient temperatures to derive the activity of carbon A_c.

10   The processing function 24 outputs the calculated activity of carbon A_c for further uses by the system 10. The activity of carbon A_c output can, e.g., be displayed, or recorded over time, or used for control purposes, or any combination of these processing uses.

15   For example, in Fig. 2, the system 10 includes a display device 48 coupled to the processing function 24. The display device 48 presents the calculated activity of carbon A_c for viewing by the operator. The display device 48 can, of course, show other desired

20   atmosphere or processing information. Alternatively, or in combination, a printer or recorder can be coupled to the processing function 24 for showing the calculated activity of carbon A_c and its fluctuation over time in a printed strip chart format.

25   In a preferred embodiment, the processor 18 further includes an atmosphere control function 46. The atmosphere control function 46 includes a comparator function 52. The comparator function 52 compares the calculated activity of carbon A_c to a desired control

30   value or set point, which the operator can supply using, e.g., an input 54. Based upon the deviation between the calculated activity of carbon A_c and the set point, the atmosphere control function 46 generates a control signal to the atmosphere source 14. The control function 46

35   generates signals, to adjust the atmosphere to establish

and maintain the calculated activity of carbon A_c at or near the set point. The control function 46 is also coupled to the device 48 to show other atmosphere or processing information. In this way, the processor 18 works to maintain atmosphere conditions optimal for the desired processing conditions.

As described above, the atmosphere used in the spherodize annealing process should prevent carburization, decarburization, and oxidation of the steel parts. In addition, the atmosphere should prevent sooting from occurring. The conditions for sooting occur when $A_c > 1$. Since sooting is a kinetically controlled process, the rate of sooting will increase with increasing values of A_c that are greater than unity.

Fig. 4 shows, based upon thermodynamic considerations, the relationship between A_c and temperature for a two phase conditions of ferrite (α-Fe) and iron carbide (Fe_3C) or ferrite (α-Fe) and austenite (γ-Fe) in the region to the left of the dotted line in Fig. 1 (for hypoeutectoid plain carbon steel). The critical temperature A_1 is at or about 1333° F.

For temperatures below temperature A_1, the phases of ferrite (α-Fe) + iron carbide (Fe_3C) are the equilibrium phases. Above temperature A_1, the equilibrium phases of ferrite (α-Fe) and austenite (γ-Fe) exist, until temperature A_3. Above temperature A_3, the stable single phase austenite (γ-Fe) exists. This is also shown in Fig. 1. The value of A_3 is a function of weight percent carbon content, as Fig.1 shows. In Fig. 4, A_3 is, for the purpose of illustration, expressed as 1440° F, which corresponds to a weight percent carbon value of .4% (see Fig. 1).

In the two phase region where ferrite (α-Fe) and iron carbide (Fe_3C) exists (i.e., below temperature A_1), the value of the activity of carbon A_c at a given

temperature is determined by the reaction and the standard free energy for the reaction, as follows:

$$Fe(\alpha) + C = Fe_3C; \Delta G_{19}^{O} \quad (19)$$
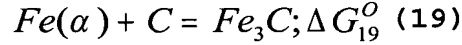
The equilibrium constant K_{19} for the reaction in Equation (19) can be expressed as follows:

$$K_{19} = \frac{A_{Fe_3C}}{A_{Fe(\alpha)}A_C} = \exp^{-\Delta G_{19}^{o}/RT} \quad (20)$$

where:

A_{Fe_3C} is the activity of iron carbide,

$A_{Fe(\alpha)}$ is the activity of ferrite.

The quantity:

$$\Delta G_{19}^{o}$$

is the standard free energy for Equation (19), expressed in calories per mole as follows:

$$\Delta G_{19}^{o} = 3,850 - 11.41T + \ln T + 9.66(10^{-3})T^2 - \frac{0.4(10^5)}{T} + 66.2T \quad (21)$$

R is the gas constant.

T is the temperature in °K.

Since, at equilibrium, $A_{Fe3C} = 1$ and $A_{Fe(\alpha)} = 1$ then:

$$A_C = \exp^{\Delta G_{19}^{o}/RT} \quad (22)$$

Equation (22) expresses the equilibrium curve shown in Fig. 4 relating A_c to temperature at temperatures below A_1. The equilibrium curve marks the transition between carburization and decarburization conditions. For a given temperature, carburization occurs for A_c values above the intersection of the equilibrium curve and the temperature. Likewise, for a given temperature, decarburization occurs for A_c values below the intersection of the equilibrium curve and the temperature.

The equation relating A_c to temperature shown in

Fig. 4 between the temperatures A$_1$ and A$_3$(where the two phases of ferrite (α-Fe) + austenite (γ-Fe) exist), is determined from the activity of austenite when in equilibrium with ferrite at temperature A$_3$. The carbon potential of the austenite at a given temperature can be ascertained using Fig. 1, from the intersection of the given temperature (on the Y-axis of Fig. 1) with the A$_3$ curve in Fig. 1. The carbon potential (on the x-axis of Fig. 1) which aligns with the temperature-A$_3$ intersection is the carbon potential for that temperature. For example, in Fig. 1, the intersection of the A$_3$ curve and the temperature 1400°F on the Y-axis, aligns with a carbon potential of 0.5 on the x-axis.

The carbon potential (expressed as a weight % carbon) of the austentite for the temperature region A$_1$ to A$_3$, as determined above, can then be used to calculate the oxygen sensor output E(mv) from the following equation, which is based upon experimental data:

$$E(mv) = A - B$$
$$where$$
$$A = 876.5 + 0.1601T - (55.75 - 0.1249T)\log C \qquad (23)$$
$$B = (25.337 + 0.05512T)\log(CO/20)$$

where:

   T is in °F.

   C is the wight percent carbon.

   CO is the carbon monoxide content, expressed as a percentage.

The A$_c$ for the temperature region A$_1$ to A$_3$ can next be determined by applying Equation (7), using the value of E(mv) as calculated from Equation (23), and also using the same value of T. Any value of CO can be used as long as the same value is used in both Equation (7) and

Equation (23). For each temperature, a similar process can be used to relate A_c to temperature for the range A_1 to A_3, resulting in the plot shown in Fig. 4 for that temperature range.

In Fig. 4, the position of the temperature line marking A_3 is a function of the weight percent carbon in the steel undergoing annealing. The $A_3 = 1440°F$ line shown in Fig. 4 corresponds to a weight percent carbon value of 0.4. The position of the A_3 line will shift to the left for weight percent carbon values above 0.4, and will shift to the right for weight percent carbon values less than 0.4.

The slope of the equilibrium curve in the region A_1 to A_3 is not affected by the weight percent carbon value. The equilibrium curve for the region A_1 to A_3 can be approximated (by a best fit analysis) by the following equation:

$$A_C = 8.975 - 0.005983T(^O F) \quad \textbf{(24)}$$

The intersection of the equilibrium curve of Equation (24) with the A_3 value for the relevant weight percent carbon value of the steel undergoing annealing marks the lowest activity of carbon value at the transition from the two phase austenite-ferrite region to a single phase austenite region.

In the temperature range between A_1 and A_3, the equilibrium curve marks the transition between carburization and decarburization. For a given temperature, carburization occurs for A_c values above the intersection of the equilibrium curve and the temperature. Likewise, for a given temperature, decarburization occurs for A_c values below the intersection of the equilibrium curve and the temperature.

Fig. 4, as generated above, shows that, for

temperatures below A_1, the preferred set point is $A_c \approx 1$, as sooting occurs as $A_c > 1$. The rate of sooting is a function of the CO content in the atmosphere. Fig. 4 also shows that the entire equilibrium curve for ferrite and iron carbide curve exists in the region where $A_c > 1$. Fig. 4 shows that, for temperatures below A_1, a decarburizing condition should be tolerated, to reduce the incidence of sooting.

For temperature conditions between A_1 and A_3, Fig. 4 shows that the entire equilibrium curve for austenite and ferrite exists in the region where $A_c < 1$. Fig. 4 shows that, for temperatures between A_1 and A_3, A_c can be maintained below 1.0 to maintain equilibrium while preventing the incidence of sooting.

For alloy steels, the magnitudes of the temperatures A_1 and A_3 depend both on the alloy elements present and the concentration of the alloy elements. Furthermore, the magnitude of the activity of carbon A_c is also affected by the type and concentration of alloy elements.

The control function 46 generates command signals based upon the comparison of the computed value A_c to the set point value. The control function 46 adjusts the mixture of gases provided by the source 14 to the furnace 12, to establish and maintain the computed value $A_c \approx 1$ at temperatures below A_1 and to maintain the computed value A_c at the value derived from Equation (24) at temperatures between A_1 and A_3.

It can therefore be seen from Fig. 4 that, for hypoeutectoid plain carbon steel, the set point A_c is a function of temperature T. The set point A_c can be assigned a generally fixed value (i.e., ≈ 1.0) at temperatures below A_1 (1333 °F). At temperatures between A_1 and A_3, the set point A_c is assigned a value determined from Equation (24).

In this way, the control function 46 works to maintain prescribed atmosphere conditions within the furnace 12 optimal for spherodize annealing in both two phase regions ferrite plus iron carbide (below temperature A_1) and ferrite plus austenite (between temperatures A_1 and A_3). By maintaining the computed value A_C at the set point value, the control function 46 prevents both carburization and sooting, while minimizing decarburization in the two phase regions.

The same control function 46 can also serve to prevent oxidation and minimize internal oxidation. The magnitude of E(mv) at a given temperature condition is indicative of the partial pressure of oxygen P_{O2} in the gas atmosphere inside the furnace 12. In the illustrated and preferred embodiment, the control function 46 compares E(mv) generated by the *in situ* oxygen sensor 22 to a threshold value, which is selected based upon experimental data to mark an oxygen condition close to the onset of oxidation at the temperature condition sensed by the *in situ* temperature sensor 20. The operator can supply the selected threshold value, e.g., using an input 66.

The relationship between E(mv) and the onset of oxidation of iron over a given range of temperatures can be experimentally determined. Fig. 5 illustrates a representative plot of the relationship based upon actual data and observation. Fig. 5 plots the E(mv) output (y-axis) over a given temperature range (°F) (x-axis). The intersection of a given temperature (on the x-axis) and the line shown in Fig. 5 identifies an E(mv) value that marks the threshold of the onset of oxidation. Signal values less than the threshold indicate the likelihood of oxidation.

For example, based upon Fig. 5, if the gas atmosphere temperature is 1200° F, the threshold

E(mv) signal value is about 1023 mv. If the E(mv) signal at that temperature is less than this threshold value, the control function 46 generates an oxidation alert alarm. The operator is thereby prompted to check for air leaks in the furnace 12 and take other corrective action to prevent oxidation.

Based on Equation (7), for a fixed value of A_c (e.g., $A_c=1$) and a constant temperature condition (which is usually the objective of the temperature controller 26), E(mv) decreases with increasing concentrations of carbon monoxide. Thus, at lower temperature conditions, it is possible to have an atmosphere that is both carburizing and oxidizing. Therefore, the oxidation alert features just described is very useful when using atmospheres with higher carbon monoxide concentrations.

Graphical User Interfaces

In the illustrated embodiment (see Fig. 6), the display device 48 provides an interactive user interface 136. The interface 136 allows the operator to select, view and comprehend information regarding the operating conditions within the spherodize annealing zone. The interface 136 also allows the operator to change metal heat treating conditions in the zone.

The interface 136 includes an interface screen 138. It can also include an audio or visual device to prompt or otherwise alert the operator when a certain processing condition or conditions arise. The interface screen 138 displays information for viewing by the operator in alpha-numeric format and as graphical images. The audio device (if present) provides audible prompts either to gain the operator's attention or to acknowledge operator actions.

The interface screen 138 can also serve as an input device, to input from the operator by conventional touch activation. Alternatively or in combination with

touch activation, a mouse or keyboard or dedicated control buttons could be used as input devices. Fig. 6 shows various dedicated control buttons 140.

The format of the interface screen 138 and the type of alpha-numeric and graphical images displayed can vary.

A representative user interface screen 138 is shown in Fig. 6. The screen 138 includes four block fields 142, 144, 146, and 148, which contain information, formatted in alpha-numeric format. The information is based upon data received from the associated heat and atmosphere controllers, relating to processing conditions within the spherodize annealing furnace 12.

The first field 142 displays in alpha-numeric format a process variable (PV), which is indicative of the activity of carbon valve A_c derived by sensing from the *in situ* sensors residing the annealing atmosphere of the furnace 12. The value displayed in the first field 142 comprises the quantity A_c derived by the algorithm 44 according to Equation (7).

The second field 144 displays in alpha-numeric format the set point value SP for the activity of carbon A_c for the given processing condition. The value displayed is received as input from the operator, as previously explained.

The third field 146 displays in alpha-numeric format the deviation DEV derived by the comparator function 52 of the atmosphere control function 52. The deviation DEV displays the difference between the process variable PV and the set point SP.

The fourth field 148 displays in alpha-numeric format the percent output (OUT), which reflects the magnitude of the control correction commanded to bring the process variable PV to the set point SP.

The screen 138 also includes two graphical block

fields 150 and 152. The fields 150 and 152 provide information about the processing conditions within a given zone of the furnace 56 in a graphical format.

The first block field 150 includes a vertically oriented, scaled bar graph. A colored bar 154 graphically shows the magnitude of the process variable PV relative to the set point on the bar graph. An icon 156 marks the set point value within the scale of the bar graph.

The second block field 152 includes a horizontally oriented, bar graph scaled between 0 and 100. A colored bar 158 graphically depicts percent output (OUT), which is the magnitude of the control correction commanded to bring the process variable PV to the set point SP, as before explained.

As Fig. 6 shows, the screen 138 also includes various other an alpha-numeric block fields 160, 162, and 164 displaying status information. The block field 160 identifies the mode of atmosphere control, e.g., AUTO (for automatic control by the processing module) or MAN (for manual). The block field 162 identifies that the annealing zone of the furnace 12 is being monitored. The block field 164 contains date and time stamp.

By selection of a control button 140, the operator can select among different display options for viewing information relating to the selected zone. For example, the operator can select a trend display (see Fig. 7), which graphically displays the variation over time of selected processing conditions, e.g., PV, E(mv), % CO, and T. As another example, the operator can select a real time data display (see Fig. 8), which records instantaneous unit data values for selected processing variables, e.g., measured temperature T, the oxygen sensor output E(mv), the % CO, and the computed A_c value, and the process set point for A_c.

The graphical user interface 136 shown in Figs.

6 to 8 can be realized using a HONEYWELL™ VPR-100 Controller with standard or advanced free form math capability (Honeywell, Inc.).

The features of the invention are set forth in the following claims.